A STUDY ON WETTABILITY PROPERTIES OF RUTILE-PHASE TiO_2 NANOSTRUCTURE FILM

SYAFA SYAHIRAH BINTI HJ. TAIB

A thesis submitted in

fulfillment of the requirement for the award of the

Degree of Master of Electrical Engineering

Faculty of Electrical and Electronic Engineering

Universiti Tun Hussein Onn Malaysia

FEBRUARY 2020

ACKNOWLEDGEMENT

In the name of Allah, the Most gracious and the Most Merciful

Firstly, I would like to express my sincerest appreciation to my supervisor, Assoc. Prof. Dr. Mohd Khairul Bin Ahmad, for his continuous support, encouragement and patience throughout the entire process. To my co-supervisors, Dr. Jais Bin Lias, I wish to express my deepest gratitude for their guidance throughout my research.

A lot of thanks to my beloved family, although you have not been literally beside me when I am finishing this thesis, you are all my motivation for everything like moral and mental support through my ups and downs. Particularly to my parents, Taib Bin Jalil (father) and Sabariah Binti Md. Top (mother), you are my strengths throughout my master studies. Thank you also to my dearest partner, Muhammad Amar Hazwan Bin Hisham, the one who always motivate me and be there when I needed.

To all my lab mates and Graduate Association Student (GSA), thank you. Even though you are not literally involved in this study, I thank you all for the moral support and bonding that I will forever treasure in my life. It was fun having all these years spent time doing craziness things with all of you.

Special thanks are given to Microeletronics & Nanotechnology - Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia (UTHM) for allowing me to use FESEM, XRD, Contact Angle Measurement (WCA) and providing me with technical support whenever needed. I would also like to acknowledge all MiNT-SRC technicians, my friends, Mrs. Faezahana and Encik Nasrul leading up to the submission of this thesis.

ABSTRACT

Titanium dioxide (TiO_2) is a very well-known material for applications such as photocatalysis, solar cell and self-cleaning applications. This material can also be coated on glass surfaces, especially for car windows and building windows as well. Glass in the market nowadays, the material that coated on the glass weakens as time passes and harmful to the environment. Since TiO_2 material has advantages such as being inert and environmentally friendly, thus the study of the wettability properties of rutile-phase TiO_2 film is introduced for self-cleaning application. TiO_2 is fabricated using the hydrothermal synthesis method at 150°C. The fluorine-doped tin oxide (FTO) is used as a substrate to grow the TiO_2 nanostructure by mixing hydrochloric acid (HCl), deionised water (DI) and titanium (IV) butoxide (TBOT). The effects of the duration of the hydrothermal process, the volume of HCl, the volume of TBOT as well as the use of surfactant hexadecyltrimethylammonium bromide (HTAB) toward the synthesis growth of nanorods are thoroughly evaluated. The samples are analysed by using X-Ray Diffraction (XRD) for structural properties, Field Emission Scanning Electron Microscopy (FE-SEM) for morphology structure and water contact angle (WCA) measurement for wettability properties. FE-SEM shows that the layer of TiO_2 nanorods is successfully grown on the FTO substrate. The contact angle results for different hydrothermal reaction times and different HCl and TBOT volumes reveal that TiO_2 has wettability properties of hydrophilicity (<90°). Even though different structures are achieved from different parameters, none of the samples exhibit hydrophobic characteristics. From the XRD data analysis, all of the samples are rutile-phase TiO_2. The optimum amount of hydrothermal reaction time, volume of HCl and volume of TBOT are at 16 hours, 130 mL and 5 mL, respectively, where TiO_2 has a crystalline structure with fine tetragonal shape and the highest contact angle. The use of HTAB have a change in wettability properties as it makes the sample become super-hydrophilic compared to as-prepared sample which is hydrophilic only.

ABSTRAK

Titanium dioksida (TiO_2) adalah bahan yang sangat terkenal untuk aplikasi seperti *photocatalysis*, sel suria dan aplikasi pembersihan. Bahan ini juga boleh disalut pada permukaan kaca terutamanya untuk tingkap kereta dan bangunan. Kaca yang berada di pasaran sekarang, bahan yang disalut pada permukaan kaca tersebut tidak tahan lama dan tidak mesra alam. Oleh kerana bahan TiO_2 mempunyai kelebihan seperti tidak aktif dan mesra alam, maka kajian penyerapan air terhadap permukaan filem TiO_2 fasa rutil telah diperkenalkan sebagai aplikasi pembersihan. TiO_2 dibuat menggunakan kaedah sintesis hidrotermal pada 150°C. *Fluorin-doped tin oxide* (FTO) digunakan sebagai substrat untuk mentumbuhkan TiO_2 nanostruktur dengan mencampurkan asid hidroklorik (HCl), air ternyahion (DI) dan *titanium (IV) butoxide* (TBOT). Kesan tempoh proses hidroterma, jumlah HCl, isipadu TBOT serta penggunaan surfaktan hexadecyltrimethylammonium bromide (HTAB) terhadap pertumbuhan sintesis *nanorods* dinilai dengan teliti. Sampel dianalisis dengan menggunakan pembelauan sinar-X (XRD) untuk sifat-sifat struktur, Mikroskop Pengimbasan Pelepasan Medan (FE-SEM) untuk struktur morfologi dan pengukuran *water contact angle* (WCA) untuk sifat pembasahan. FE-SEM menunjukkan lapisan nanorod TiO_2 berjaya ditumbuhkan di atas substrat FTO. Hasil daripada sudut air untuk masa tindakbalas hidrotermal, HCl dan TBOT yang berbeza mendedahkan bahawa TiO_2 mempunyai sifat penyerapan air yang hidrofilik (<90°). Walaupun struktur yang berbeza dicapai daripada parameter yang berlainan, tidak ada sampel yang menunjukkan ciri hidrofobik. Daripada analisis data XRD, semua sampel adalah TiO_2 dalam fasa rutil. Jumlah optimum masa tindakbalas hidrotermal, HCl dan jumlah TBOT masing-masing adalah 16 jam, 130 mL dan 5 mL, di mana ia mempunyai struktur kristal dengan bentuk tetragonal halus dan sudut tertinggi. Penggunaan HTAB mempunyai perubahan dalam sifat penyerapan di mana ia membuat sampel menjadi sifat super-hidrofilik berbanding sampel yang tersedia yang mempunyai sifat hidrofilik sahaja.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C	-	Degree Celsius
°	-	Degree
DI	-	Deionised water
FE-SEM	-	Field Emission Scanning Electron Microscope
FTO	-	Fluorine-doped tin oxide
HCl	-	Hydrochloric acid
HTAB	-	Hexadecyltrimethylammonium Bromide
ITO	-	Indium-doped tin oxide
µm	-	Micrometer
nm	-	Nanometer
TBOT	-	Titanium (IV) butoxide
TiO_2	-	Titanium dioxide
TCO	-	Transparent coating oxide
UV	-	Ultraviolet
WCA	-	Water contact angle
XRD	-	X-ray diffractometer

CHAPTER 1

INTRODUCTION

1.1 Background Study

Glass has been used for many purposes such as windows for automotive and buildings as well as decorative tableware. The main setbacks of normal glass are that it is prone to be dusty and the formation of fog may hinder the transparency of the glass. Previous research by Kume and Nozu from Japan in 1985 stated that sheet glass coated with titanium dioxide (TiO_2) has the ability to stay clean by rapidly and automatically decomposing and removing organic stains adhered to the glass surface [1]. Most importantly, the contact angle made by a water droplet on the glass is reduced as a function of UV irradiation time and the observation is involved as part of their patent application. This seems to be the first clear claim of a photo-induced super-hydrophilicity effect related to titanium films on glass due to the removal on the surface of hydrophobic organic stains.

Fluorine-doped tin oxide (FTO) will act as a substrate, where titanium dioxide (TiO_2) will furthermore be fabricated on its surface. The slight resemblance between rutile TiO_2 and FTO properties gives an advantage toward the growth of the nanostructure because the small lattice mismatch between the FTO substrate and rutile TiO_2 renders the epitaxial growth of compact rutile TiO_2 layer on the FTO glass [2]. FTO is one of the examples of Transparent Conducting Oxide (TCO) with excellent conductivity, high optical transparency and low reflectance in the visible waveband (about 400–800 nm), chemical stability, the ability to endure high temperature, corrosion resistance, non-toxicity and low cost [3]–[5].

TiO_2 may be synthesised in different types of nanostructures such as nanorods [6], nanotubes [7], nanoflowers [8], nanobelts [9] and nanostrawberry [10], [11]. The different types of nanostructures can be used in various applications and fields such as thermoelectricity [12] and photocatalysis [1]. The formation of nanostructured TiO_2 is highly dependent upon the synthetic technique applied in the fabrication process such as hydrothermal [13], DC magnetron sputtering [14], electrochemical anodization [13], solvent gel electrolyte [15], screen printing [16] and spin coating [17]

In this study, the hydrophilicity and hydrophobicity of TiO_2 thin film surface are characterised by using the water contact angle (WCA) measurement. A water contact angle of greater than 150^o will give high repellence and water striders that is able to roll off the water freely, while <5° has better adsorption-type material where the water spreads to the surface completely, leaving no water droplets. The surface of the thin film needs to have high surface roughness and low chemical energy in order to have a better hydrophobic form, while for hydrophilic, it is *vice versa* [18]. The highest contact angle can give a super-hydrophobic form, in which the droplet water can bounce back from the surface, as in Figure 1.1. Meanwhile, the lowest contact angle is known as super-hydrophilic. Therefore, it will give an advantage in self-cleaning application and other practical applications such as anti-corrosion [19], anti-icing [20], oil-water separation [21] and drag-reduction [22].

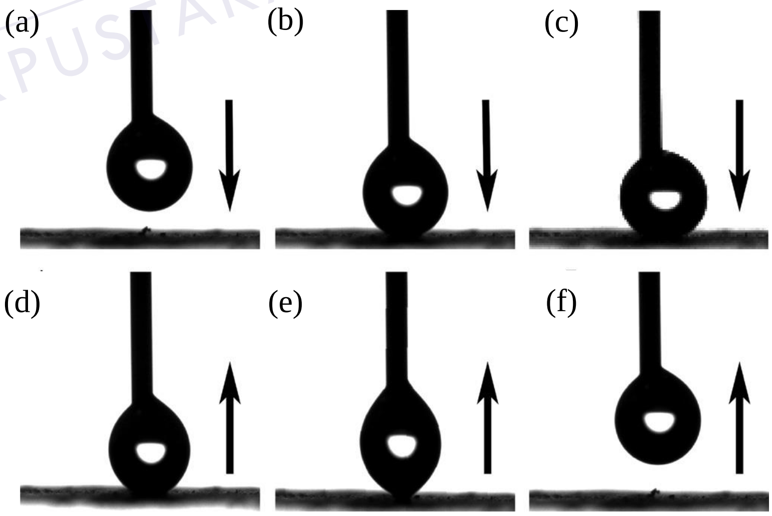

Figure 1.1: Sequential photographs of a 4-µL water droplet (a) suspended on a syringe, (b) slightly and (c) tightly contacting the as-prepared super-hydrophobic surface and departing from the surface (d–f). The arrows represent the syringe's moving direction [23]

In a recent study, it is found that the enhancement of the hydrophobicity of rutile-phase TiO_2 nanostructure can be achieved by using the hydrothermal method [24]. Hydrothermal method is the most preferable method since it can grow the rutile-phase TiO_2 nanostructures at low temperature [2]. Therefore, it is a suitable method for this project.

1.2 Problem Statement

Nanostructures with unique surface wettability have long served as a source of inspiration for scientists and engineers. Materials with extreme wetting characteristics such as super-hydrophilic and super-hydrophobic surfaces have drawn significant attention due to their prospective use in multiple applications such as self-cleaning fabrics, anti-fog windows, anti-corrosive coatings, drag-reduction systems and effective water transport. In engineering, developing surface wettability by manipulating chemical properties, structural properties and morphological properties is an important aspect to study for self-cleaning applications.

However, self-cleaning applications have weak points, such as the material used is not always easy to fabricate, the long-term durability of the coating material itself weakens as time passes and the chemical used is harmful. In previous studies, titanium dioxide has been used with additional chemicals such as polystyrene [25], polydimethylsiloxane [26] and polyethylene [27], and this will increase the use of harmful chemicals by the consumers and will eventually harm the environment.

Therefore, the use of simple material and simple fabrication for self-cleaning glass consisting of TiO_2 could be a perfect solution. The hydrothermal technique has benefits in controlling the nanorods' development effectively. In addition, TiO_2 is a non-poisonous, unreactive material, is easy to deal with and is not dangerous to its surroundings. Since TiO_2 has many advantages for the environment and has the ability to be used in self-cleaning applications, for instance, as an anti-fogging substance [28], therefore this project is proposed to study the wettability properties of the surface of rutile TiO_2 film. Wettability properties of TiO_2 nanorods film will enhance the hydrophobicity and hydrophilicity of TiO_2 film's properties.

1.3 Research Objectives

The objectives of this project are:

1. To fabricate aligned TiO_2 nanorods via hydrothermal method.
2. To characterise the morphological and structural properties of nanorods toward wettability properties.
3. To investigate the wettability properties of TiO_2 rutile nanostructures using water contact angle (WCA) measurement.

1.4 Research Scope

In order to fulfil the stated objectives, the scope of this project includes:

1. Fabricate aligned TiO_2 nanostructure using hydrothermal method at 150 ℃.
2. The surfactant used is hexadecyltrimethylammonium bromide (HTAB).
3. The optimisation of parameters are subjected to hydrothermal duration (8, 12, 16 and 24 hours), volume of hydrochloric acid (120, 130, 140 and 160 mL) and amount of precursor (4, 5 and 6 mL).
4. The characterisations of the synthesised TiO_2 thin film are carried out by using Field Emission Scanning Electron Microscopy (FE-SEM) image, X-ray diffraction (XRD) and water contact angle (WCA) measurement for surface morphology, structural properties and contact angle for wettability properties, respectively.

CHAPTER 2

LITERATURE REVIEW

This chapter contains the summary and reviews related to this research work. The summary is about nanostructure, hydrophobic titanium oxide, existing work and experimental research which can be associated with the proposed project. The previous studies contribute to the principles and thoughts in this research whilst the experimental studies help gain a better understanding of this study. A specific and similar approach is used to discover, select and evaluate all the research related to a specific query.

2.1 Substrate Preparation for Fabrication

Transparent conducting oxide (TCO) was first reported by Badeker and published in 1907, which reports that thin films of oxidised Cd metal become transparent while remaining electrically conducting when deposited in a glow discharge chamber. The global market for this thin film has since then been recognised. The list of potential TCO materials include tin-doped indium oxide, In_2O_3:Sn (ITO); fluorine-doped tin oxide, SnO_2:F (FTO); antimony-doped tin oxide, SnO_2:Sb (ATO) and aluminium-doped zinc oxide, ZnO:Al (AZO) [29].

It has been found that the application of TCOs in large quantities is application-specific; for instance, it is widely used in architectural glass applications and heat-efficient windows that can reflect in the IR region [29], [30]. Its application in home appliances, for instance, is for a stove which uses transparent conducting thin film to maintain parameters such as the outside temperature for the transparent window to remain safe for touch. In addition, transparent conducting oxide also works with electrochromic material for automobiles in the automotive industries, for instance in dimming rear-view mirrors automatically [31].

As a summary of this project, the FTO thin film is used as the substrate in the experiment. Compared to other thin films, FTO is more inexpensive. It is very stable and has been used in a wide range of applications such as UV sensor [23], [32], photovoltaic application [33], wastewater purification, energy-saving windows [34] and insulating application [4]. Based on previous studies, the surface morphology of the FTO thin film is rougher than the ITO thin film, where the FTO thin film is smooth with some scratches as shown in Figure 2.1 [35]. For the nanostructures, the FTO is useful to growth the nanorods due to the lattice mismatch between the FTO and the rutile nanorods. The lattice mismatch between the tetragonal FTO (a = b = 0.4687 nm) and rutile TiO2 (a = b = 0.4594 nm) is 2%. This small lattice mismatch may promote the epitaxial nucleation and growth of rutile TiO_2 nanorods on FTO which is give a better substrate compared to normal glass. Since FTO thin film is well known for its advantages, therefore it is very suitable to use it as a glass substrate in this project.

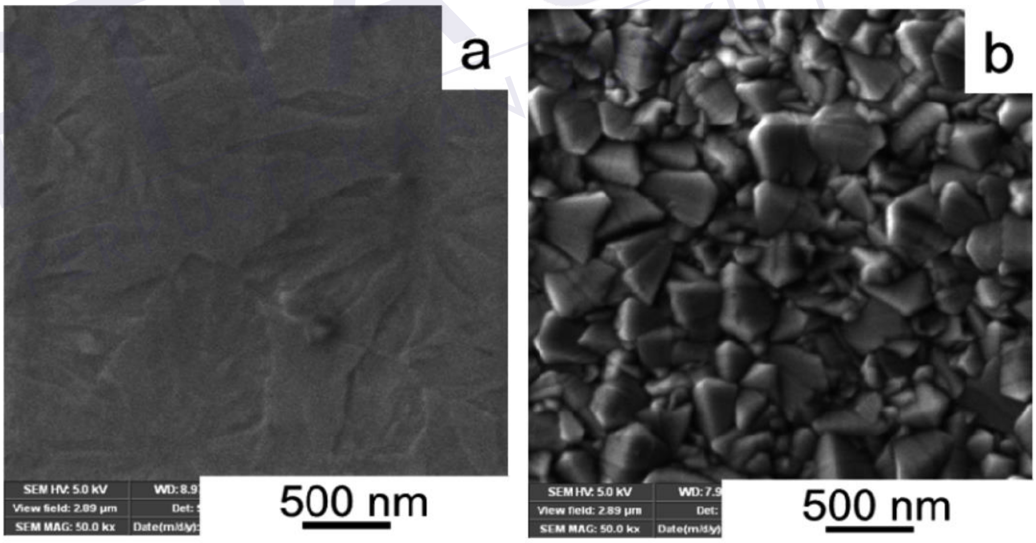

Figure 2.1: FE-SEM images of the (a) ITO and (b) FTO electrodes [35]

2.2 Previous Studies on Titanium Dioxide

Titanium dioxide is the most researched single-crystalline framework in the surface science of metal oxide. Single-crystalline TiO_2 surfaces have a wide range of applications and the expectations of the surface properties on the fundamental level will enhance to improve materials and devices in many fields. Examples of the use of TiO_2 are in heterogeneous catalysis, as a photocatalysis, in solar cells for the generation of hydrogen and electrical energy, as a white pigment (e.g., in cosmetics), and as a coating in corrosion-protection, in foodstuffs, and in electric devices as a varitors [36].

The applications of titanium dioxide have been discovered by some recent related research on its properties. One of the most significant uses of TiO_2 is its use for photodegradation with the help of organic molecules. Titanium dioxide is a semiconductor, and the electron-hole pair that is made upon irradiation with sunlight may separate, resulting in charge carriers. These charge carriers may migrate to the surface where they react with adsorbed water oxygen to produce radical species. From that, it will attack any adsorbed organic molecules, resulting in complete decomposition into CO_2 and H_2O. Some of the applications from this process range from the purification of wastewaters and disinfection based on the bactericidal properties of TiO_2, to applications in self-cleaning coatings on car windshields. Titanium dioxide also works to slow or stop the growth of tumour cells by the injection of TiO_2 in rats and with subsequent near-UV illumination [37].

There are three phases of TiO_2 crystallite nanostructure, which are anatase, rutile and brookite. Anatase and brookite are metastable and can be transformed into the rutile phase when annealed at high temperatures [38], [39]. On the other hand, rutile is TiO_2's most stable form. Temperatures around 700°C and above are commonly used to produce pure TiO_2 rutile structure. It is reported that the temperature at the beginning of the transition should be around 600°C to transform anatase into rutile, as shown in Figure 2.2 [40].

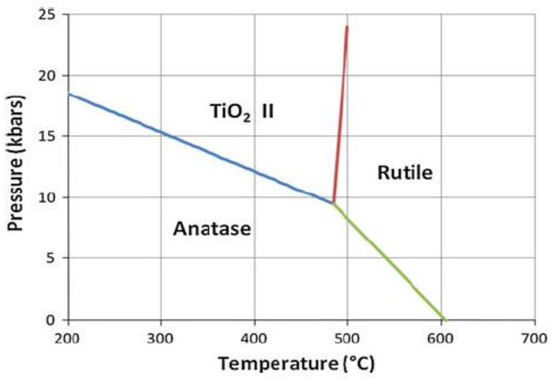

Figure 2.2: Reaction boundaries of phase transition in TiO_2 [40]

Anatase's crystal structure consists of sharing 4 edges while rutile consists of sharing 2 edges. This is because anatase and rutile contain 4 and 2 atoms per unit cell [40]. The structures of both anatase and rutile are tetragonal. Depending on the shape, the band gap energy for TiO_2 is large, at about 3.0 eV. The specific values for anatase and rutile are 3.26 and 3.05 eV, respectively [38], [41], [42]. The difference is attributed to its structural arrangement, as shown in Figure 2.5 [40].

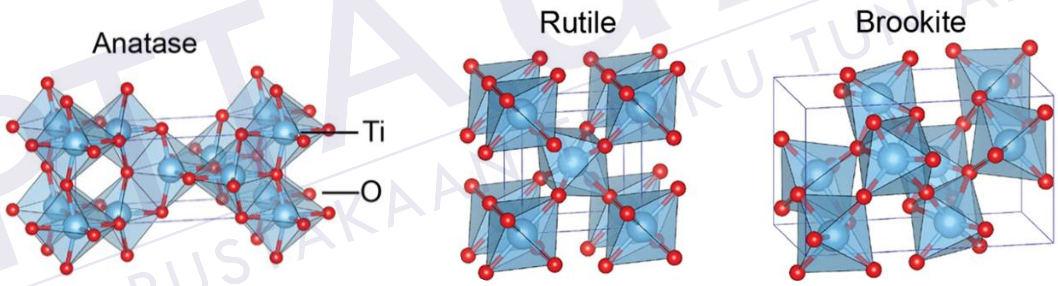

Figure 2.3: Crystal structures of TiO_2 rutile (tetragonal, $P4_2/mmm$), brookite (orthorhombic, Pbca) and anatase (tetragonal, $I4_1/amd$) polymorphs [43]

2.2.1 Applications of TiO_2 Surface

TiO_2 is globally known nowadays for its useful characteristics. Most of them are well known for applications such as dye-sensitised solar cell (DSSC), chemical sensor, photocatalysis, thermoelectricity and wastewater treatment. This is supported by a study that has been using TiO_2 material as Batik wastewater treatment. It is stated that TiO_2 has the ability to remove toxic elements, can be recycled and is easy to produce [44]. The surface found on the TiO_2 thin film is a grain form.

Another experiment conducted a study of photocatalytic activity by using doped TiO_2 with different Lanthanum (La) contents. The effects show that La dopant has a first-rate inhibition on the TiO_2 phase transformation and does not provide upward thrust to a brand new PL signal, but it may enhance the intensity of the photoluminescence (PL) spectra with a suitable La content, attributed to the increase within the content of the surface oxygen vacancies and defects [45]. Table 2.1 is the summary from previous studies on applications of TiO_2 surface.

Table 2.1: Summary of previous studies on applications of TiO_2 surface

Application	**Apply on**	**Result**
Self-cleaning [46][47][48][49]	• Mirrors, window glasses, windshields of automobiles	- TiO_2–SiO_2, anti-fogging ability - TiO_2–Al_2O_3, high water repellent [28]
Anti-corrosion [50][51]	• Metal	- Strong corrosion resistance in 0.01% HCl solution for a couple of days
Electricity [33], [34], [52], [53], [54], [55]	• Dye-sensitised solar cell	- Recent research do not reach more than 10% efficiency outside laboratory environment
Photocatalysis [56][57][58]	• Wastewater treatment	- Higher photocatalytic activity of anatase nanocrystalline TiO_2 was obtained as compared with rutile TiO_2[59]

2.3 Fabrication of TiO_2 Film

There are various ways to fabricate TiO_2 thin films, such as spray pyrolysis, sol-gel and electrolyte. Below is a summary of methods that previous researcher used in their experiments.

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